

Episodic Particle Transport Events Controlling PAH and PCB Cycling in Grand Traverse Bay, Lake Michigan

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To evaluate the influence of episodic events on particle and hydrophobic organic contaminant (HOC) cycling in the Great Lakes, we deployed sequencing sediment traps at two locations in the western arm of Grand Traverse Bay, Lake Michigan. The traps collected integrated samples of settling particles every 2 weeks from May 1997 to September 1999. The total polycyclic aromatic hydrocarbon (t-PAH) and total polychlorinated biphenyl (t-PCB) settling fluxes from the surface waters in the southern site were significantly greater than those from the northern site. In addition, there were more frequent brief increases in the mass flux to the southern site than to the northern site. These episodic events, which occurred only 20% of the time, accounted for 65% of both the mass flux and t-PAH flux. The t-PCB flux was not influenced by these episodic events, and only 18% of the t-PCB flux occurred during these events. PAHs and PCBs appear to be tracing different types of particles in the water column. Several large mass flux events characteristic of seiches were observed simultaneously in the benthic nepheloid layer (BNL) at both the northern and the southern sites. The particles settling as a result of these resuspension events had lower t-PCB and t-PAH concentrations than particles settling at other times. This suggests that the material settling into the traps on the high mass flux days is composed of a mixture of the less contaminated underlying resuspended sediment and the "regular" contaminant-rich particles settling into the BNL.

Introduction

Hydrophobic organic contaminants (HOCs) entering the Great Lakes water column in the dissolved phase readily partition onto settling particles. The residence time of HOCs in the water column is controlled by the fate of the particulate matter (1). Over long time scales, particles are removed from the water column and buried in the sediment. However, the short-term dynamics of aquatic systems are more complex. Surficial sediment is susceptible to resuspension, and the HOCs bound to the particles can be re-injected into the water column (2). Tracer studies using ²³⁹Pu and ¹³⁷Cs clearly illustrate the fate of particulate-bound chemicals in the water column (3, 4). Over 95% of these tracers are removed

from the water column and buried in the sediment within a few years (3). However, when sediment is resuspended, a small fraction of the tracers desorb from the particles and are released back into the water column. The process of sediment resuspension and redeposition is responsible for continual low levels of ²³⁹Pu and ¹³⁷Cs observed in the water column (4). Several studies suggest that the water column concentrations of PCBs and some PAHs are also influenced by resuspension and focusing (5–12).

In the Great Lakes, particulate matter rapidly settles through the water column and accumulates in the benthic nepheloid layer (BNL). However, most of the material in the BNL is not incorporated into the underlying bottom sediment (5). Sediment trap studies conducted in Lake Superior found that 90% of the t-PCBs and low molecular weight PAHs in the water column settled to within 5 m of the bottom, but only 1–35% of them accumulated in the sediment (6, 9). Instead, material in the BNL can be recycled back into the water column or transported to other locations (13). For example, in 1983 the fall overturn in Lake Superior mixed the PCB-enriched BNL throughout the water column and increased the net residence time of PCBs in the lake (13). Resuspension events during an abnormally severe winter in 1979 caused an elevated inventory of PCBs in Lake Superior (14).

The episodic resuspension and subsequent transport of surface sediment and BNL material profoundly influences biogeochemical processes in coastal waters. Episodic events (e.g., storms, spring runoff) are brief events during which a large amount of material settles through the water column. They can be caused by storm-induced sediment resuspension events or the settling of phytoplankton blooms. Episodic events are transient in nature and difficult to predict and study. Previous sediment trap studies conducted in the Great Lakes found that the resuspension and vertical mixing of the sediment and the benthic nepheloid layer (BNL) throughout the water column primarily occurs during the winter unstratified months (5, 9, 12). However, these studies sampled the settling particles on the time scales of months and did not have the sufficient temporal resolution needed to observe the influence of episodic events. Sequencing sediment traps that sample the settling particles for days or weeks have been used in the Great Lakes to observe resuspension events during the unstratified period. In Lake Ontario, several local resuspension events were observed during November and December of 1992 using sequencing sediment traps (8). The temporal resolution of sequencing sediment traps facilitates the study of episodic events.

If episodic resuspension events mix contaminated sediment back into the water column, they could potentially reintroduce contaminants back into the food web. On the other hand, if the resuspended material has a lower contaminant concentration than the water column, the particles could potentially scavenge the contaminants from the water column. The PCB concentration of the material settling into the sediment traps deployed by Hawley et al. (8) in Lake Ontario decreased during the resuspension events relative to the other sampling periods. This suggested that the source of material in the traps during these events was depleted in PCBs. The authors utilized this information combined with other data to trace the input of particles to Lake Ontario from the Niagara River during resuspension events. The impact of these episodic resuspension events on contaminant cycling depends on the source of material. In this study, we deployed sequencing sediment traps to collect settling particles continually every 2 weeks for 2 years in order to observe the

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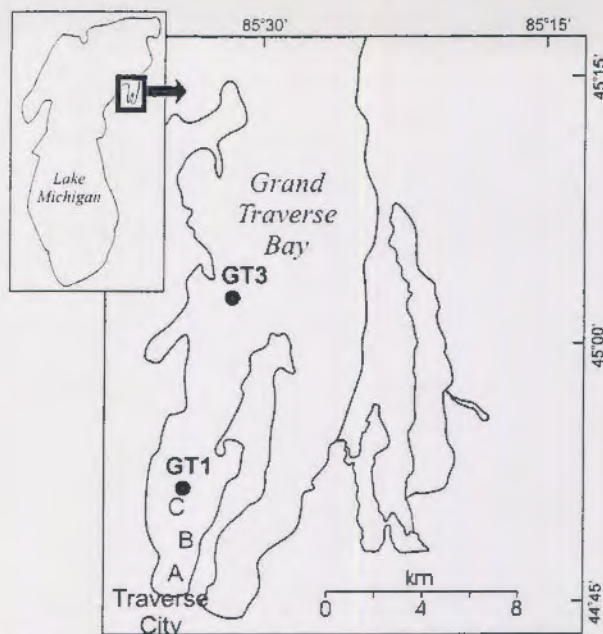


FIGURE 1. Location of sequencing sediment traps deployed in Grand Traverse Bay, Lake Michigan. ● = sediment trap location, and A, B, and C = locations of surficial sediment grab (see Table 2).

influence of episodic events on PCB and PAH cycling in Grand Traverse Bay, Lake Michigan.

Methods

Sample Site. Grand Traverse Bay is located in northeastern Lake Michigan (Figure 1) and was selected as the study site because its water column characteristics are similar to the open waters of northern Lake Michigan but it is more accessible for sampling. A peninsula separates the southern portion of the bay into two narrow arms with fjord-like bathymetry and circulation (15). The two arms of the bay are each approximately 2.5 km wide and reach depths of over 100 m. The results presented in this paper are part of a larger project currently being conducted in Grand Traverse Bay to examine the seasonal cycling of HOCs within the water column, and determine the factors influencing bioaccumulation of HOCs in the food web (16–19).

Sampling Description. Sequencing sediment traps were deployed at two locations in the western arm of the bay (Figure 1). The traps collected integrated samples of the settling particles initially every week and then every 2 weeks from May 1997 to August 1999. The first series of sediment traps were deployed off the R/V Shenehon in May 1997 and collected integrated samples every week until September 1997. These initial traps were then retrieved, and new sequencing traps were placed in the water column at the same location. These traps collected samples of the settling particles every 2 weeks from September 1997 to September 1998. At the end of 1 year, these traps were retrieved, and a final set of sediment traps were deployed from September 1998 to August 1999.

The sequencing sediment traps used in this study had an aspect ratio of 8:1 above the funnel. A detailed description of the collection efficiency of these traps can be found in ref 20. For each deployment period, 23 60-mL polyethylene bottles were positioned on a computer-controlled carousel near the base of the trap. At the preprogrammed sampling intervals, a new bottle rotated under the base of the trap. Prior to deployment, each bottle was filled with 6 mL of chloroform to prevent microbial degradation of the settling material and 55 mL of deionized water. At both sites, the

surface traps were placed at a depth of 30 m to capture the settling particles just below the thermocline. At GT1 and GT3, the bottom traps were deployed at depths of 91 and 115 m, respectively, to capture the settling particles 5 m above the lake floor.

In addition to deploying the sediment traps, the water column at each site was characterized from April to September of both 1997 and 1998 using an SBE-25 conductivity, temperature, and depth profiler (CTD) equipped with Sea Tech fluorometer and transmissometer sensors (SeaBird, Electronics Inc.). To further characterize the water column, ~200 L water samples were collected for PCB and PAH analysis during the 1997 CTD deployments, and each time the sediment traps were deployed (18, 20). A detailed description of the water sampling procedure and results is presented in other papers related to this study (16–18). In addition, three surficial sediment samples were collected using a ponar grab in a transect from our study sites to Traverse City (19, 21).

Sample Handling and Analysis. For a detailed description of the sample handling procedure and analysis method, see reference (21). After the sediment traps were retrieved, the polyethylene bottles were placed in a cooler filled with ice until they were transported to the Great Lakes Environmental Research Laboratory in Ann Arbor. A liquid/liquid extraction using chloroform and hexane was used to determine the PAH and PCB analyte concentrations (21). Prior to extraction, the samples were spiked with the following PAH and PCB surrogate standards: fluorene-*d*₁₀, fluoranthene-*d*₁₀, perylene-*d*₁₂, 3,5-dichlorobiphenyl (IUPAC #14), 2,3,5,6-tetrachlorobiphenyl (IUPAC #65), and 3,3',4,4',5,6-hexachlorobiphenyl (IUPAC #166). Twenty-five PAHs were quantified in all sediment trap samples using a Hewlett-Packard (HP) model 5890 gas chromatograph connected to an HP 5972 Mass Selective Detector using electron ionization in the SIM mode. To quantify PCB analytes in these samples, the extract was eluted through deactivated precleaned Florisil columns (21). PCB analytes were collected from the first fraction with petroleum ether while a second fraction was eluted from the Florisil columns (21). Total PCBs (48 resolved congeners and 58 unresolved congeners) were quantified using an HP model 5890 gas chromatograph equipped with a ⁶³Ni electron capture detector (21).

Analytical Quality Assurance. Laboratory blanks and field blanks were extracted along with the samples. Field blanks consisted of the contents of sediment trap polyethylene vials which did not rotate under the funnel to collect settling particles and that were spiked with surrogate PAHs and PCBs. These blanks were analyzed to determine if the chloroform extracted analytes from the polyethylene vials and water column during deployment. The average field blank had a t-PAH mass of 12 ± 5 ng (*n* = 10) and a t-PCB mass of 9 ± 3 ng (*n* = 10). Laboratory blanks consisted of 6 mL of chloroform and 55 mL of deionized water spiked with surrogate PAHs and PCBs. The average laboratory blank had a t-PAH mass of 8 ± 3 ng (*n* = 10) and a t-PCB mass of 5 ± 2 ng (*n* = 10).

A conservative blank correction method was used to ensure that the concentration of PAH and PCBs was not overestimated. The method detection limit (MDL) was defined as 3 times the average concentration of both field blanks and laboratory blanks and was calculated for each sample based on the mass of the sample. If a PCB or PAH concentration did not exceed 3 times the average blank concentration, the analyte was considered nonquantifiable and removed from the results. For t-PAHs, the MDL of all of the samples ranged from 5 to 660 ng/g depending on the mass of the sample. The average sample t-PAH concentration was 9 times greater than the MDL or 27 times greater than the blanks. For PCBs, in addition to the MDL evaluation, a

TABLE 1. Summary of the Mass, t-PAH, and t-PCB Flux Results from GT1 and GT3

site (trap depth)	mass flux, g/m ² -day		t-PAH flux, ng/m ² -day		t-PCB flux, ng/m ² -day	
	average	range	average	range	average	range
GT1 surface stratified (30 m)	0.53	0.01–0.96	230	20–860	30	10–100
GT1 surface unstratified (30 m)	1.5	0.15–5.5	3550	70–18400	30	10–90
GT1 bottom (91 m)	2.4	0.01–13	1020	NQ to 3900	60	NQ to 170
GT3 surface stratified (30 m)	0.50	0.01–1.2	180	NQ to 1220	20	NQ to 60
GT3 surface unstratified (30 m)	0.9	0.04–4.2	180	NQ to 730	10	NQ to 50
GT3 bottom (115 m)	7.1	0.03–24	620	NQ to 1900	90	NQ to 300

congener representing over 35% of the total was considered nonquantifiable and removed from the results. This correction was made because PCBs were produced in mixtures and the percentage of a single congener in the mixture did not exceed 35% of the total. The average sample was 3.5 times greater than the MDL or 10.5 times greater than the blank. The MDL of all the samples ranged from 0.2 to 115 ng/g of t-PCBs depending on the mass of the sample.

In all, 142 samples were analyzed for PAHs and PCBs. Average percent recoveries for the surrogates in all the samples were 72 ± 15 and 78 ± 16 for PCB congeners 14 and 166, respectively, and 69 ± 15 , 76 ± 14 , and 77 ± 13 for fluorene-*d*₁₀, fluoranthene-*d*₁₀, and perylene-*d*₁₂, respectively. NIST Standard Reference Material 1941a (sediment) extracted with this method resulted in PAH recoveries ranging from 65 to 101%, indicating that this extraction successfully extracts "native" contaminants from the sediment trap samples.

Results

Water Column Characteristics. During April and May of 1997 and 1998, the temperature and fluorescence profiles at both GT1 and GT3 were uniform throughout the water column, indicating the water was vertically well mixed. There was a long cold spring in 1997, and the surface water temperatures did not begin to rise until mid-June, whereas 1998 was a warmer year and the surface water temperature was elevated by the beginning of June (18). Between June and August of both years, the surface temperature continued to rise, and the water column was vertically stratified. During this time, the thermocline reached a maximum depth of around 20 m. By the beginning of September, the surface temperature had reached its maximum, and the water column remained thermally stratified through mid-September (18). Transmittance profiles during stratification show the continual presence of a benthic nepheloid layer in the bottom 5–10 m of the water column (18).

Mass Flux from the Surface Waters. The mass flux results are briefly summarized here for comparison with the contaminant data and are discussed in detail in reference (20). For the entire duration of the sampling period, the mass flux from the surface waters at the southern site (GT1) ranged from 0.16 to 5.5 g/m²-day and had a time-weighted average of 1.1 g/m²-day. The time-weighted flux was calculated by first multiplying the mass flux of each sample by the number of collection days for the sample. Then, the results of this calculation for each sample were added together and divided by the total number of collection days for all the samples to determine the time-weighted flux. At the northern site, GT3, the time-weighted average mass flux was 0.9 g/m²-day and ranged from 0.04 to 4.2 g/m²-day. During the stratified period (June–September), the time-weighted average mass fluxes from GT1 and GT3 were 0.5 and 0.4 g/m²-day, respectively. During the unstratified period (October–May), the time-weighted average mass fluxes were 1.5 and 1.1 g/m²-day at GT1 and GT3, respectively (Table 1), a 3-fold increase relative to the stratified period.

The average mass fluxes in the stratified period at both GT1 and GT3 are similar to the average mass fluxes of 0.65

± 0.26 and 0.50 g/m²-day observed in southern and central Lake Michigan (Table 1) (3, 7). The mass flux observed in Grand Traverse Bay and open Lake Michigan during the stratified period is roughly 6 times greater than the 0.14 ± 0.06 g/m²-day mass flux observed during the stratified period in the open waters of Lake Superior (9). During the unstratified period, the mass flux of 1.5 g/m²-day observed in sediment traps deployed in central Lake Michigan was similar to the average mass fluxes of 1.5 and 1.1 g/m²-day observed at GT1 and GT3, respectively (7). In southern Lake Michigan, the sediment traps were placed in a zone of maximal deposition during the unstratified period and had an average mass flux of 6.5 ± 0.6 g/m²-day, approximately 4.5 times greater than the unstratified mass flux observed in GTB (3).

Detailed analysis of the mass flux data is provided in ref 20 and briefly summarized here. The temporal trends in mass flux do not coincide between the two sites (Figure 2). Several brief large mass flux events were observed during the unstratified period at both GT1 and GT3. However, the frequency and extent of these events were greater at GT1 than at GT3. The brief high mass flux episodic events account for most of the annual mass settling into the traps. The surface trap mass flux data suggest that particle transport in GTB is a complex process driven by brief episodic events.

A study by Smith (15) used the homogeneous case of the linear barotropic equations to simulate the general circulation pattern in Grand Traverse Bay during the unstratified period. This study found that wind-driven circulation creates a clockwise rotating gyre in the southern portion of the western arm (15). If a similar gyre rotated during the course of this study, it would effectively isolate the particulate matter reaching GT1 from GT3 and could produce the episodic events observed at GT1. Analysis of wind data collected at the Traverse City Airport suggests that particles settling from GT1 are not transported to GT3. Wind impulse (speed \times duration) for southerly winds shows a slight correlation with mass flux from GT1 ($r^2 = 0.18$, $n = 61$) but not GT3 ($r^2 = 0.005$, $n = 61$), indicating winds out of the south resuspend enough materials in the shallow southern end of Grand Traverse Bay to reach GT1 but not GT3.

Mass Flux in the Benthic Nepheloid Layer. The near-bottom sediment traps were deployed at depths of 91 and 115 m at the southern and northern site, respectively, and stopped rotating in December of 1997. At GT1, the southern site, the mass flux ranged from 0.01 to 13 g/m²-day with a time-weighted average of 2.4 g/m²-day. At GT3, the time-weighted average was 7.1 g/m²-day, and the flux ranged between 0.03 and 24 g/m²-day (Figure 3; Table 1). The mass flux to GT3 was an average of 3 times greater than the mass flux to GT1. Two large resuspension events dominated flux at both sites, one in late summer and the other in early December, which caused both traps to stop rotating. Unlike at the surface, the bottom trap mass flux events were synchronized, suggesting bay-wide influences on BNL circulation. However, the difference in scale of the resuspension events indicates local conditions are important in determining the extent of resuspension.

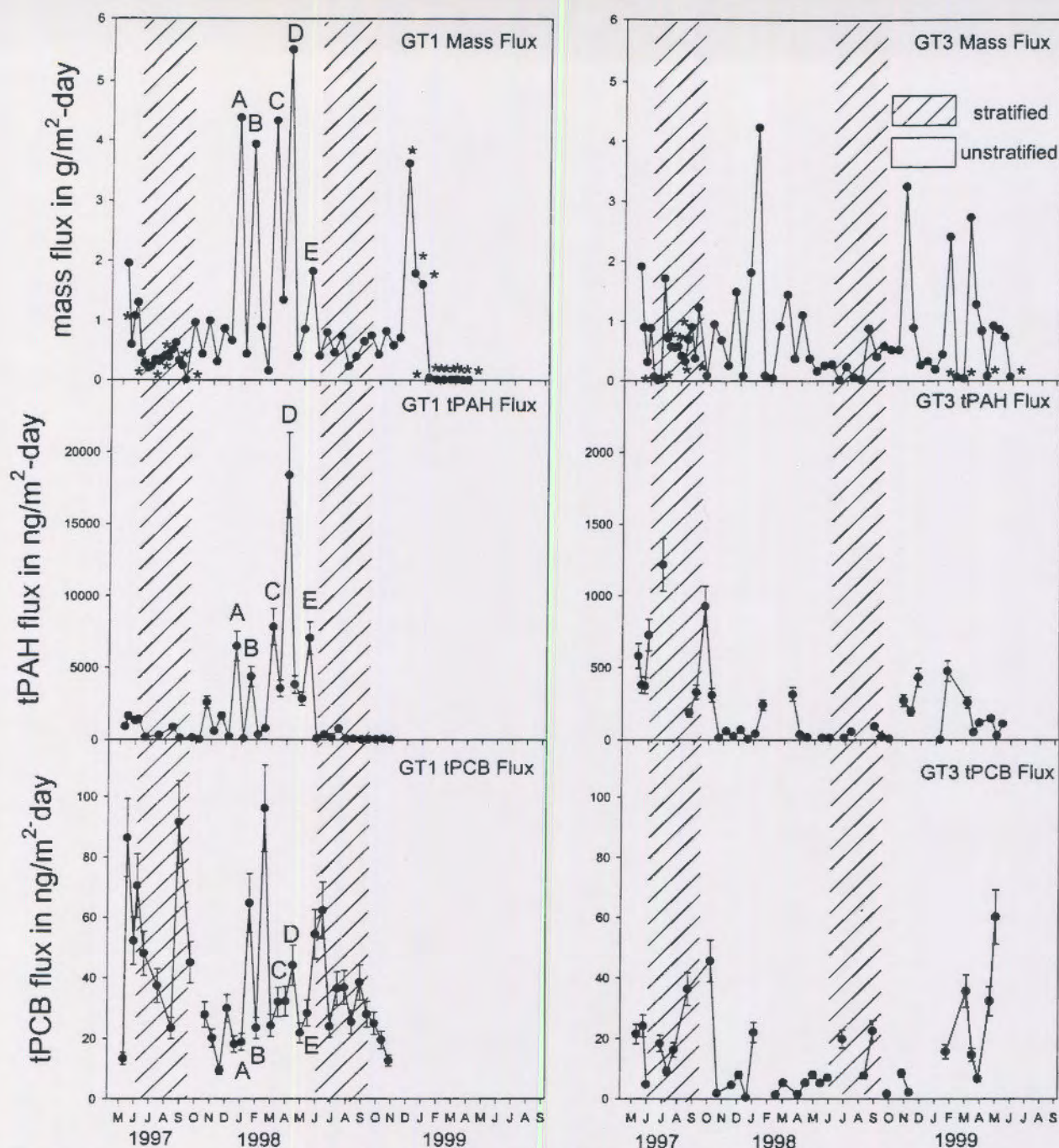


FIGURE 2. Mass, t-PAH, and t-PCB flux from the surface traps at GT1 and GT3. Note the 10× difference in scale for t-PAH flux from GT1 and GT3. Samples with PAH and PCB levels below method detection limits were not plotted on the graph. Asterisks indicate samples collected but not analyzed for PAHs and PCBs.

The large resuspension event observed at both sites in late summer did not produce a corresponding increase in the mass flux from the surface traps. The water column was stratified during this event, and the resuspended particles did not cross the thermocline. The surface traps collected settling particles from the thermocline and showed no indication of the resuspension event in the bottom waters. On the other hand, the December resuspension event occurred when the water column was unstratified. This event produced a corresponding increase in the mass flux from the surface waters at both GT1 and GT3 in the 2 week sampling period following the failure of the traps. This observation suggests that the winter resuspension events remixed the BNL throughout the water column. However,

since the traps stopped rotating after this event, more data are needed to confirm this finding.

The episodic events in the surface traps were much shorter in duration than those observed in the bottom traps. In the surface traps, the mass flux fluctuated greatly every 2 weeks, and the high mass flux episodic events may even have occurred on 1 day in the 2 week sampling interval. In contrast, the bottom trap large episodic events lasted for more than 2 weeks. The differences in mass flux between the surface and bottom waters suggest that there are different forcing factors influencing particle transport in surface and bottom waters.

t-PAH Flux from the Surface Waters. At the southern site, the t-PAH flux ($\Sigma 25$ PAHs) ranged between 20 and 18 400

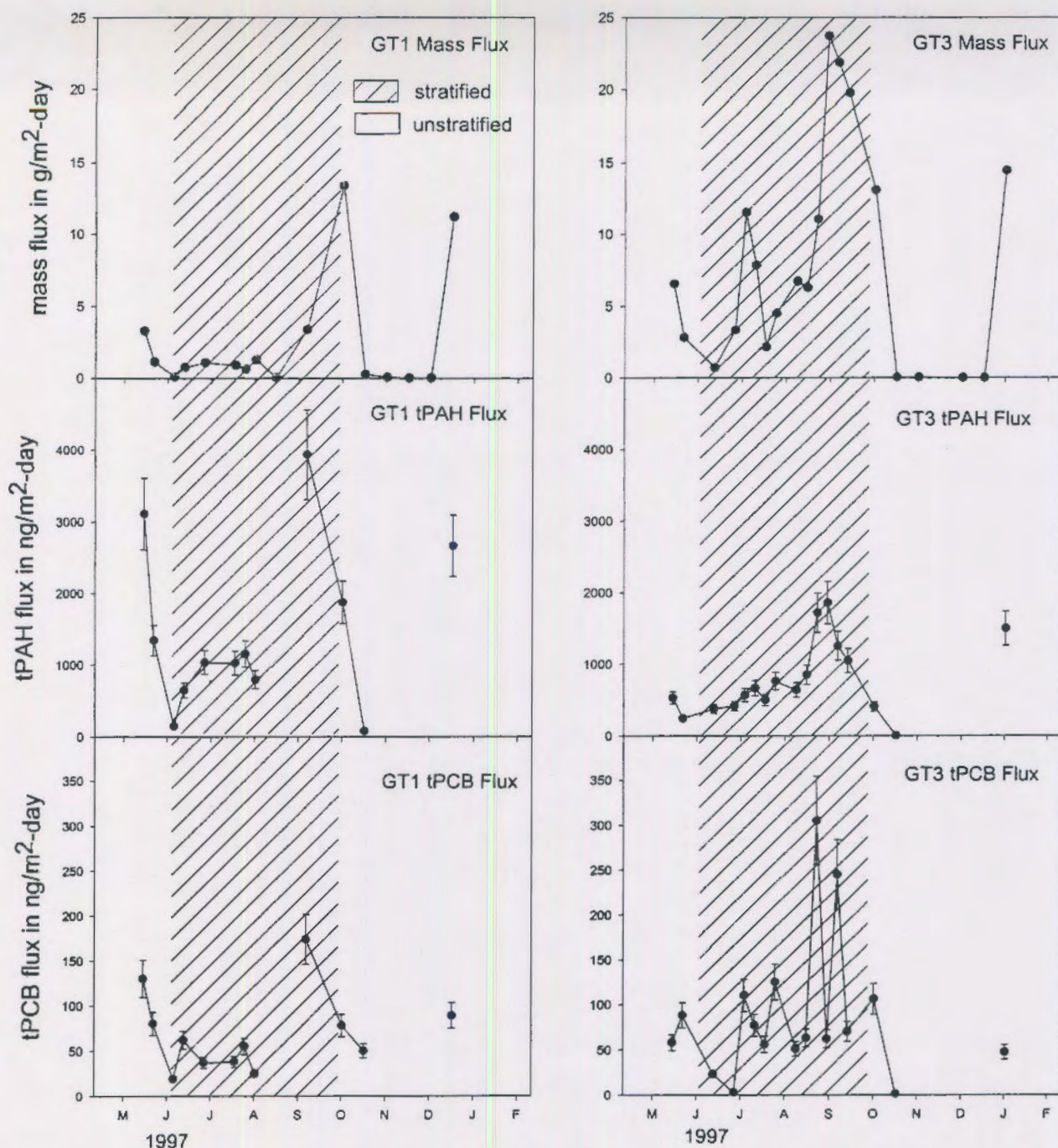


FIGURE 3. Mass, t-PAH, and t-PCB settling fluxes to the bottom traps at GT1 and GT3. Sampling dates without t-PAH and t-PCB fluxes were below method detection limits.

ng/m²-day, with a weighted average of 2160 ng/m²-day (Table 1). At the northern site, the t-PAH flux was an average of 12 times lower than at GT1 and ranged from nonquantifiable (due to the small amount of material settling into the sediment trap) to 1220 ng/m²-day, with a weighted average of 180 ng/m²-day (Figure 2). However, a t-test performed after log-transforming the data so that they were normally distributed indicates there is no significant difference in t-PAH flux between GT1 and GT3 during the stratified period ($\alpha = 0.05$; Table 1). The difference in annual t-PAH flux between the two sites is due to the t-PAH flux difference during the unstratified period (Table 1). The time-weighted average t-PAH flux at GT1 during the unstratified period was 2960 ng/m²-day, or 17 times greater than the weighted average mass flux to GT3 of 180 ng/m²-day during the same time

period. The t-PAH fluxes observed in this study are lower than the fluxes in Lake Superior in 1985 and 1991 (Table 1) (6, 9). In Siskiwit Lake, t-PAH fluxes averaged 270 ng/m²-day (22), in the Mediterranean Sea t-PAH fluxes range between 300 and 900 ng/m²-day (23), and in a small rural lake in the United Kingdom t-PAH fluxes averaged 32 000 ng/m²-day (12).

GT1 is close to Traverse City (~2 km) and appears to be influenced by local combustion of fuels during the winter months. The concentration of t-PAHs on the settling particles is significantly greater in the unstratified period than during the stratified period ($\alpha = 0.05$, Figure 4). In contrast, GT3 is ~12 km north of Traverse City and away from urban influence. At this site there was no seasonal variation in the concentration of t-PAHs on settling particles. Unlike with PCBs, the

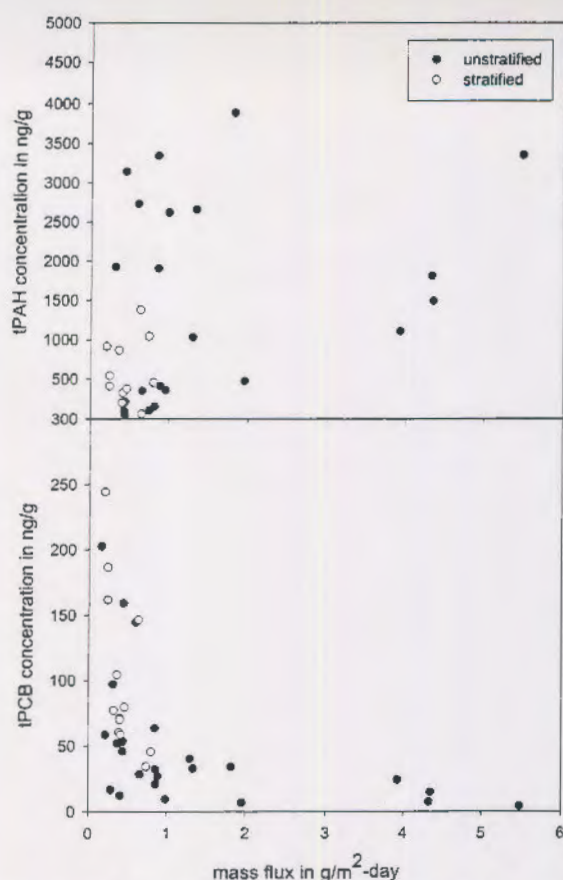


FIGURE 4. Variation in PAH and PCB concentration with mass flux from the surface traps at GT1 during the stratified and unstratified periods. For comparison, the surficial sediment t-PCB concentration was 30 ng/g, and the concentration of t-PCBs on the suspended solids ranged from 10 to 70 ng/g. The surficial sediment t-PAH concentration was 3700 ng/g, and the suspended solids t-PAH concentration ranged from 700 to 4670 ng/g.

concentration of PAHs on the settling particles is poorly correlated with mass flux (Figure 4). There is no systematic variation in PAH flux with changes in mass flux. This lack of coordination could suggest there are multiple sources of particles to this site and they all differ in their PAH concentrations.

GT3 was used to compare our results to those of previous sediment trap studies in Lake Superior conducted during the stratified period (6, 9) since this northern site is less influenced by local anthropogenic activity. Jeremiason et al. (9) noted a significant decrease in the phenanthrene and fluorene settling flux from 1984 to 1991 in Lake Superior; however, the flux of all other PAH compounds was relatively constant. To quantify the rate of decline of both phenanthrene and fluorene, an exponential decay model was fitted to the flux of these compound. In 1984, the phenanthrene flux in Lake Superior was 660 ng/m²-day, and the fluorene flux was 40 ng/m²-day. In 1991, the fluxes were 130 and 7 ng/m²-day for phenanthrene and fluorene, respectively, resulting in a first-order decrease for both phenanthrene and fluorene fluxes of 0.17 year⁻¹. In this study, the fluxes of the two compounds were 70 and 4 ng/m²-day. Overall, both the phenanthrene and fluorene fluxes decreased with a first-order constant, which is comparable to the corresponding Lake Superior fluxes corrected for the long-term rate of decline of 0.17 year⁻¹.

t-PAH Fluxes in the Benthic Nepheloid Layer. At GT1, the t-PAH flux to the bottom traps ranged between nonquantifiable (due to the low amount of material settling into

the sediment trap) and 3900 ng/m²-day, and the time-weighted average t-PAH flux was 1020 ng/m²-day. At GT3, the weighted-average t-PAH flux to the bottom traps was 620 ng/m²-day and ranged from nonquantifiable to 1900 ng/m²-day (Table 1). Despite having a higher average mass flux, a log-transformation of the data indicates the average t-PAH settling flux to the bottom trap GT3 was not significantly different from the t-PAH flux to GT1 ($\alpha = 0.05$). At both sites, the large mass flux episodic event peaks correspond temporally to increases in t-PAH fluxes (Figure 3).

t-PCB Flux from the Surface Waters. The southern site, GT1, and the northern sites, GT1 and GT3, had weighted-average t-PCB fluxes of 30 and 10 ng/m²-day, respectively. The t-PCB flux at GT1 ranged from 10 to 100 ng/m²-day, and the t-PCB flux at GT3 ranged from nonquantifiable (due to the small amount of material settling into the sediment trap) to 50 ng/m²-day at GT3 (Table 1). The episodic events captured in the surface traps at GT1 did not correspond to increased t-PCB fluxes because the t-PCB concentration decreased proportionally during these events (Figure 4). The concentration of t-PCBs on the settling particles is inversely related to mass flux. Therefore, unlike with t-PAHs, the t-PCB concentration was highest during the stratified period when mass flux was lowest. This difference in concentration is probably due to the diatom and flagellate settling that occurs during the stratified period. This material is rich in organic carbon, and its low mass flux is a result of its low specific gravity (24). PCBs readily partition onto particles enriched in organic matter (25), thus increasing the concentration of PCBs on the settling particles during the stratified period.

Data from GT3 were used to compare our results to those of other northern Great Lakes studies since it is the more northern site analyzed in this study and the least influenced by local anthropogenic inputs. Sediment trap studies conducted on Lake Superior found that the flux of t-PCBs decreased from 1980 to 1992 with a first-order rate loss constant between 0.20 and 0.26 year⁻¹ from 1980 to 1992 (9, 26). To compare the PCB flux in Grand Traverse Bay to those of other studies, the impact of the long-term decline must be considered. In 1991, the particles settling out of the upper 35 m of the Lake Superior water column had a t-PCB flux of 48 ± 23 ng/m²-day (9). Accounting for the decline in PCB flux, the t-PCB settling flux observed by Jeremiason et al. (9) in Lake Superior in 1997 is estimated to be between 5 and 21 ng/m²-day if the study was conducted in 1997. This number is in good agreement with the average t-PCB surface trap settling flux of 10 ng/m²-day observed at GT3. The t-PCB settling flux measured in this study is comparable to the 1994 flux of 17 ± 10 ng/m²-day measured in an oligotrophic lake in Canada (10) and lower than the t-PCB fluxes measured in sediment traps deployed in the 1980's and early '90's in Lake Superior and Lake Ontario (5, 9, 27).

t-PCB Flux to the Benthic Nepheloid Layer. The t-PCB flux to the bottom traps ranged from nonquantifiable to 170 ng/m²-day at GT1, and the weighted average t-PCB flux was 60 ng/m²-day. At GT3, the t-PCB flux to the bottom traps ranged from nonquantifiable to 300 ng/m²-day, and the weighted average was 90 ng/m²-day (Figure 4, Table 1). Even though the surface trap t-PCB flux was 3 times greater at GT1, a log-transformation of the data and subsequent *t*-test confirm that the bottom trap fluxes are not significantly different between sites ($\alpha = 0.05$).

Differences Comparing t-PAH and t-PCB Fluxes. PAHs and PCBs appear to be tracing different types of particles in the water column. This difference probably reflects the different emission histories of the two contaminants. PAHs are emitted to the atmosphere primarily bound to particulate matter, and many do not readily repartition in the environment (28). As a result, the fate of PAHs is closely linked to the transport of particulate matter in the water column.

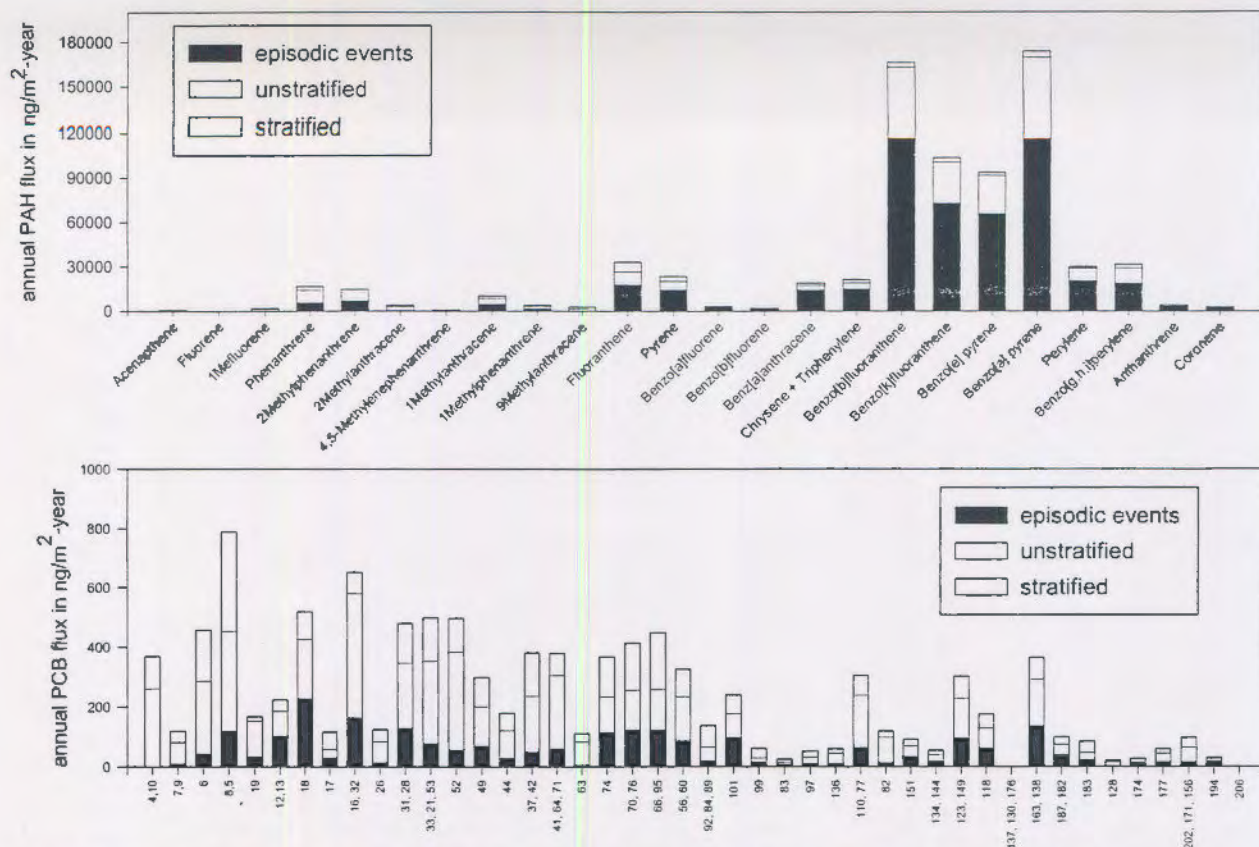


FIGURE 5. Contribution of episodic events to the annual fluxes of PAHs and PCBs settling from the surface water at GT1.

Increases in mass flux from the surface waters and to the BNL at both sites corresponded to increases in the t-PAH flux. In contrast, PCBs were not emitted with combustion particles, and the t-PCB flux appears to be more influenced by partitioning onto settling particles than is the t-PAH flux. Despite the lower mass flux during the stratified period, the stratified flux and unstratified t-PCB flux at both sites are not significantly different. Although organic carbon content data are not available for these samples, our results suggest that seasonal variability in the concentration of t-PCBs on the settling particles is primarily influenced by changes in the particles' compositions. Previous sediment trap studies found that particles with a high organic carbon content settle during the stratified period, resulting in high t-PCB flux even when the overall mass flux is low (3). In the BNL, the organic carbon content on the settling particles does not vary significantly with season (3), and increases in mass flux corresponded to increases in the t-PCB flux. Our results are consistent with variations in the organic carbon levels observed in other Great Lakes studies.

Spatial Differences. The main differences between the two sites occurred during the unstratified period, implying there is minimal particle transport from GT1 to GT3 during this time period (Table 1). This finding is consistent with the model generated by Smith (1973) which found that a gyre rotating in the southern portion of the western arm minimized particle transport to the north during the unstratified period (15). Additionally, wind impulse is positively correlated with mass flux at GT1 but not GT3, indicating that the particles settling at GT1 are not transported to GT3. Results from this study suggest there is a source of t-PAHs coming from Traverse City during the unstratified period that do not reach GT3.

Discussion

Episodic Events. The surface trap mass flux at GT1 was dominated by five episodic events during the unstratified period. The mass flux episodic event peaks, denoted by letters A–E in Figure 2, correspond temporally to peaks in the t-PAH flux but not the t-PCB flux. These events occurred 20% of the time and account for 65% of the total mass flux collected during the 18 month deployment. During these episodic events, 65% of the total t-PAH flux and 18% of the total t-PCB flux settled from the surface waters (Figure 5). To further evaluate the influence of episodic events, the fluxes were divided into three categories: stratified, unstratified, and episodic events, and the data were log-transformed so that they became normally distributed. For the t-PAH flux, a one-way ANOVA showed these three periods were significantly different, and a subsequent Tukey/Kramer analysis found that this difference is due to the episodic events. The PAH fluxes during the stratified and unstratified period were not significantly different at the 95% confidence interval. A similar analysis was conducted with the t-PCB flux. In this case, there was no significant difference in the t-PCB fluxes during the three periods (Figure 5). This suggests that the source of material to the traps during the episodic events is enriched in PAHs relative to PCBs.

Potential sources of episodic event particles include near-shore resuspension and transport, local resuspension, phytoplankton blooms, and riverine transport. There is little evidence that either phytoplankton blooms or riverine transport is a major source of material settling from the surface waters in Grand Traverse Bay. CTD casts observed several phytoplankton blooms without ever noting significant increases in the mass flux. This occurs because, as mentioned previously, the settling fluxes did not correspond to periods of maximum phytoplankton biomass, as determined by CTD

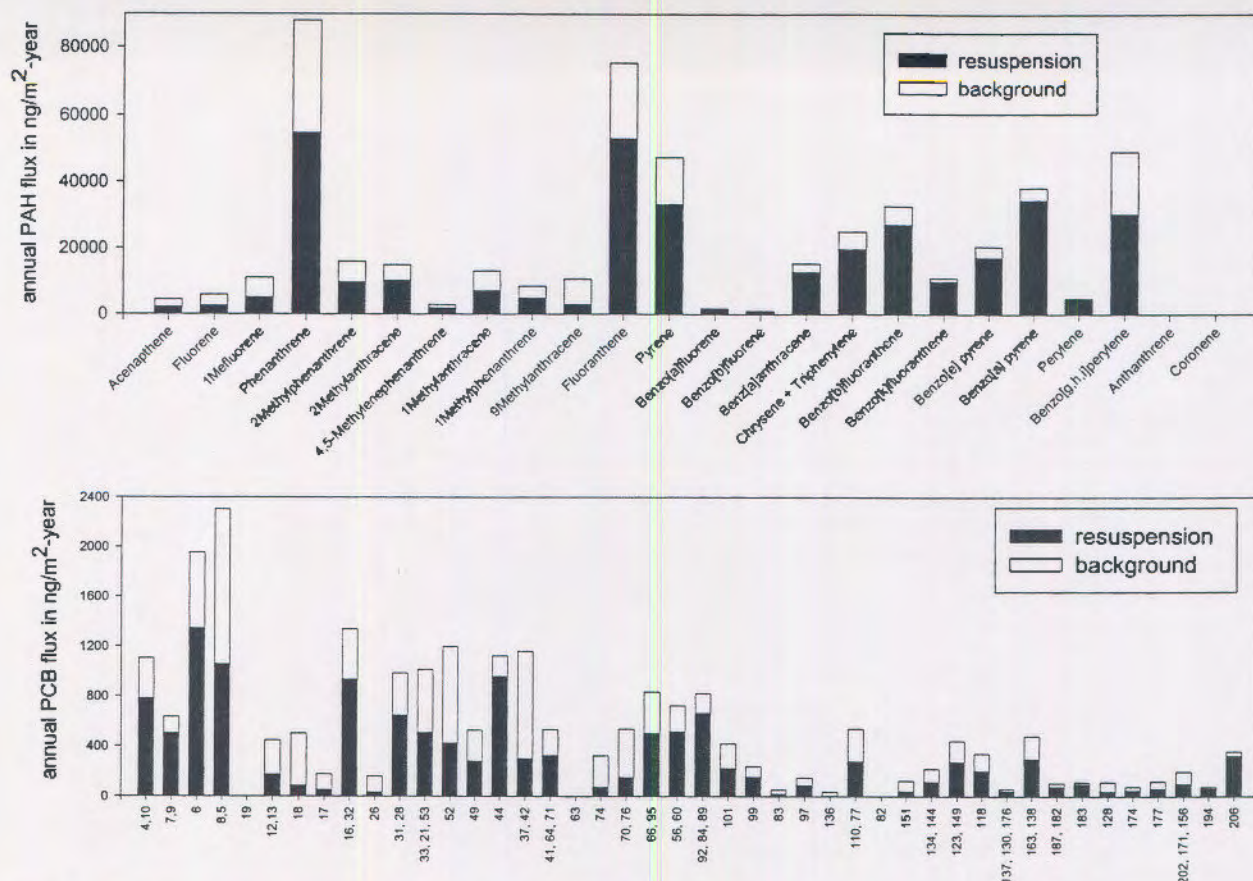


FIGURE 6. Contribution of resuspension events to the annual PAH and PCB fluxes to the BNL at GT1.

TABLE 2. Ratio of t-PAH/t-PCB in the Sediment and Sediment Traps

site	t-PAH/t-PCB ratio	depth (m)	location
A (near Traverse City)	760	30	44°46.70' N, 85°36.52' W
B (midway to Traverse City)	350	49	44°47.52' N, 85°36.42' W
C (near GT1)	100	96	44°49.50' N, 85°36.93' W
GT1 sediment traps			44°50.50' N, 85°36.82' W
episodic events	180	30	
unstratified	42	30	
stratified	7	30	
bottom trap	16	91	

profiles. The specific gravity of phytoplankton is low, and the plankton blooms apparently do not produce large mass settling fluxes in this system (24). The Bordman River is the only river flowing into the western arm of GTB, and its flow is controlled by a dam. The majority of particulate matter carried by the river settles out on the upstream side of the dam and never enters GTB. Near-shore resuspension and subsequent transport as well as local resuspension are the most likely sources of material settling into the traps during episodic events.

To further analyze the source of material to the surface water traps, three surficial sediment samples were collected from GT1 southward, toward Traverse City (Table 2). The near-shore sediment had higher concentrations of t-PAHs but not t-PCBs compared to sediment collected near GT1 (21). The ratio of t-PAHs/t-PCBs in the samples was used to investigate the source of material to the sediment traps during

episodic events. Both the sediment samples and the episodic event particles were greatly enriched in t-PAHs relative to t-PCBs (Table 2). The ratio of t-PAHs/t-PCBs on the episodic event particles was over 50% greater than the ratio on the sediment from the trap site and over 10 times greater than the ratio on benthic nepheloid particles. Additionally, the ratio of t-PAHs/t-PCBs of the episodic event particles was over 4 times greater than the ratio on the unstratified period particles and over 20 times greater than the ratio on the stratified period particles (Table 2). Results from this comparison suggest near-shore sediment was transported to GT1 during episodic events. If a simple linear mixing model is created for the episodic event particles based on the t-PAH/t-PCB ratio, these particles are composed of 50% of the sediment midway to Traverse City and 50% of resuspended BNL material (Table 2). This indicates that resuspension of near-shore sediments and resuspension of BNL material each contribute half of the particles to these episodic settling events (Table 2).

Benthic Nepheloid Layer Resuspension Events. Currents were measured in the western arm of Grand Traverse Bay for a short period of time using an Acoustic Doppler Current Profiler (20). However, the current profiler was removed shortly before the large resuspension events occurred. Although we do not have any current meter data during the resuspension events, the temporal synchronization of the bottom trap mass flux events at GT1 and GT3 as well as the burst-like nature of these events suggests that seiches undulate through the western arm of GTB. Burst-like increases in the mass flux similar to the large spikes we observed have been associated with seiche-induced motion in the benthic boundary layer in other studies (29, 30). According to Smith's model, the seiches motions of Lake Michigan drive internal waves running longitudinally through

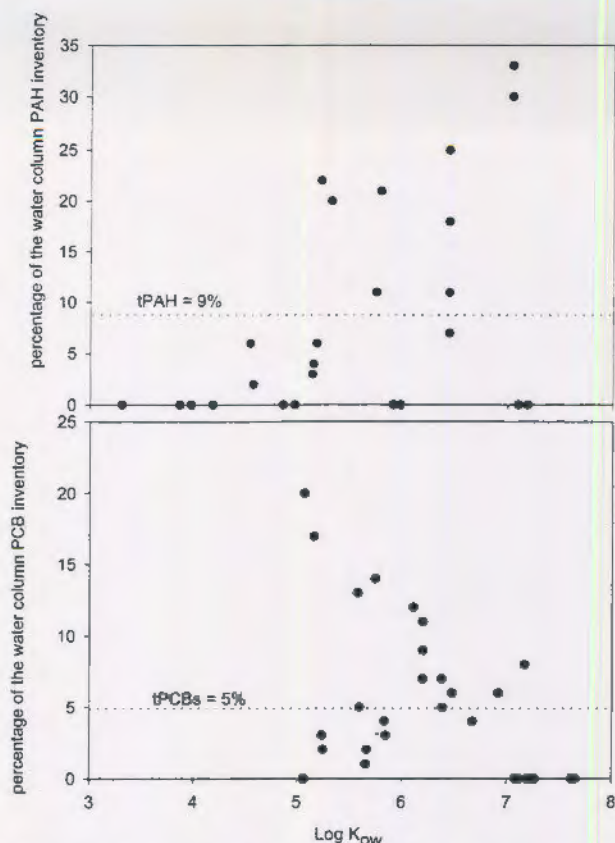


FIGURE 7. Percentage of the water column PAH and PCB inventory resuspended during the highest mass flux day at GT1.

Grand Traverse Bay and the bottom topography of the bay channels the flow of these waves through the deeper fjord-like regions of the bay (15). This movement could account for the large mass flux events observed in the bottom traps.

To evaluate the source of particles to the bottom traps, the data were log-transformed to be normally distributed and divided into two groups: high mass flux samples (resuspension events) and low mass flux samples (background). Both the t-PAH and t-PCB fluxes were greatest on the high mass flux resuspension days (Figure 6); however, the concentrations of the two HOCs on the settling particles were significantly lower on the high mass flux days than on the low mass flux days ($\alpha = 0.05$). This suggests that the additional material settling into the traps during the resuspension events is less contaminated with t-PCBs and t-PAHs than the background material settling into the traps.

To evaluate the impact of these resuspension events on contaminant cycling, the amount of contaminant resuspended during the highest mass flux day was compared to the water column inventory (dissolved + particulate) of PAHs and PCBs. Since the water column inventory of PAHs and PCBs was the same at both sites, only the results from GT1 are presented. To calculate the amount of contaminant (ng/m²) added to the water column during a resuspension event, the flux of the contaminant (ng/m²-day) was multiplied by the number of collection days. The water column inventory was computed by multiplying the concentration of the contaminant (ng/m³) by the depth of the water column (m). Since we had many water column samples (16–18), the average of particulate and dissolved concentration was used for these calculations.

The t-PAH inventory in the water column is 630 $\mu\text{g}/\text{m}^2$, and the amount of material resuspended on the highest mass flux day was 25 $\mu\text{g}/\text{m}^2$ or 4% of the t-PAH inventory. Results from this calculation indicate that resuspension events are

not adding large amounts of t-PAH to the water column. However, the settling particles have a larger proportion of high molecular weight (HMW) PAHs than the water column, and resuspension events contribute up to 30% of the water column inventory of HMW PAHs (Figure 7). The influence of resuspension events also varied among the PCB congeners (Figure 7). The water column inventory of PCBs was 15 $\mu\text{g}/\text{m}^2$, and 8% of the total inventory (1.2 $\mu\text{g}/\text{m}^2$) of PCBs was resuspended during the highest mass flux day. However, the high mass flux resuspension event added up to 20% of the inventory of some of the lower molecular weight PCB congeners to the water column. Though resuspension events occur infrequently, they can add significant amounts of contaminants back into the water column. The maximum resuspension conditions evaluated in these calculations increased the water column inventory of contaminants by as much as 30%.

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Literature Cited

- (1) Eadie, B. J.; Robbins, J. A. In *Sources and Fates of Aquatic Pollutants*; Hites, R. A., Eisenreich, S. J., Eds.; Advances in Chemistry Series 216; American Chemical Society: Washington, DC, 1987; pp 319–364.
- (2) Eadie, B. J.; Vanderploeg, H. A.; Robbins, J. A.; Bell, G. L. In *Large Lakes: Ecological Structure and Function*; Tilzer, M. M., Serruya, C., Eds.; Springer-Verlag: Berlin, 1990; pp 196–209.
- (3) Eadie, B. J.; Chambers, R. L.; Gardner, W. S.; Bell, G. L. *J. Great Lakes Res.* **1984**, *10* (3), 307–321.
- (4) Robbins, J. A.; Eadie, B. J. *J. Geophys. Res. [Oceans]* **1991**, *96* (C9), 17081–17104.
- (5) Baker, J. E.; Eisenreich, S. J. *J. Great Lakes Res.* **1989**, *13* (1), 84–103.
- (6) Baker, J. E.; Eisenreich, S. J.; Eadie, B. J. *Environ. Sci. Technol.* **1991**, *25* (3), 500–509.
- (7) Eadie, B. J.; Robbins, J. A.; Landrum, P. R.; Rice, C. P.; Simmons, M. S.; McCormick, M. J. *Technical Memorandum GLERL-045*; National Oceanic and Atmospheric Administration: Ann Arbor, MI, 1983.
- (8) Hawley, N.; Wang, X.; Brownawell, B.; Flood, R. J. *Great Lakes Res.* **1996**, *22* (3), 707–721.
- (9) Jeremiason, J. D.; Eisenreich, S. J.; Baker, J. E.; Eadie, B. J. *Environ. Sci. Technol.* **1998**, *32*, 3249–3256.
- (10) Jeremiason, J. D.; Eisenreich, S. J.; Paterson, M. J.; Beaty, K. G.; Hecky, R.; Elser, J. J. *Limnol. Oceanogr.* **1999**, *44* (3), 889–902.
- (11) Jeremiason, J. D.; Eisenreich, S. J.; Paterson, M. J. *Can. J. Aquat. Sci.* **1999**, *56*, 650–660.
- (12) Sanders, G.; Taylor, J. H.; Jones, K. C. *Environ. Sci. Technol.* **1996**, *30*, 2958–2966.
- (13) Baker, J. E.; Eisenreich, S. J.; Johnson, T. C.; Halfman, B. M. *Environ. Sci. Technol.* **1985**, *17*, 854–861.
- (14) Capel, P. D.; Eisenreich, S. J. *J. Great Lakes Res.* **1985**, *11*, 447–461.
- (15) Smith, E. Ph.D. Dissertation, University of Michigan, Ann Arbor, MI, 1973.
- (16) Stapleton, H. M.; Masterson, C.; Skubinna, J.; Baker, J. E.; Ostrom, P.; Ostrom, N. *Environ. Sci. Technol.* **2001**, *35*, 3287–3293.
- (17) Stapleton, H. M.; Skubinna, J.; Baker, J. E. *J. Great Lakes Res.*, in press.
- (18) McCusker, E. M.; Ostrom, P. H.; Ostrom, N. E.; Jeremiason, J. D.; Baker, J. E. *Org. Geochem.* **1999**, *30*, 1543–1557.
- (19) Schneider, A. R.; Stapleton, H. M.; Cornwall, J.; Baker, J. E. *Environ. Sci. Technol.* **2001**, *35*, 3809–3815.
- (20) Eadie, B. J.; Miller, G. S.; Lansing, M. B.; Winkleman, A. G. *Technical Memorandum GLERL-115*; National Oceanographic and Atmospheric Administration: Ann Arbor, MI, 2001.
- (21) Cohen, A. R. M.S. Thesis, University of Maryland, College Park, MD, 2001.
- (22) McVeety, B. D.; Hites, R. A. *Atmos. Environ.* **1988**, *22*, 511–536.
- (23) Lipiatou, E.; Marty, J. C.; Salot, A. *Mar. Chem.* **1993**, *44*, 43–54.
- (24) Scavia, D.; Fahnenstiel, G. L. *J. Great Lakes Res.* **1987**, *13*, 103–120.

- (25) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley & Sons: New York, 1993.
- (26) Jeremiason, J. D.; Hornbuckle, K. C.; Eisenreich, S. J. *Environ. Sci. Technol.* **1994**, *28*, 903-924.
- (27) Oliver, B. G.; Charlton, M. N. *Environ. Sci. Technol.* **1984**, *18*, 903-908.
- (28) Harte, J.; Holdren, C.; Schneider, R.; Shirley, C. *Toxics A to Z: A guide to everyday pollution hazards*; University of California Press: Berkeley, 1991; p 479.
- (29) Shteinman, B.; Eckert, W.; Kaganowsky, S.; Zohary, T. *Water, Air, Soil Pollut.* **1997**, *99*, 123-131.
- (30) Gloor, M.; Wuest, A.; Munich, M. *Hydrobiologia* **1994**, *284*, 59-68.

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